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EVALUATION OF SILVER-EXCHANGED ZEOLITES UNDER DEVELOPMENT BY UNIVERSITY OF MAINE FOR CHEMICAL WARFARE AGENT DECONTAMINATION APPLICATIONS

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PREFACE

The work described in this report was started in November 2005 and completed in July 2006. This effort is for the evaluation of a non-toxic photo-catalytic decontamination technology based on silver-exchanged zeolites being developed by the University of Maine research team under the direction of Dr. Howard H. Patterson, Professor, Department of Chemistry, University of Maine, for the destruction of chemical warfare agents.

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EVALUATION OF SILVER-EXCHANGED ZEOLITES UNDER DEVELOPMENT
BY UNIVERSITY OF MAINE FOR CHEMICAL WARFARE AGENT
DECONTAMINATION APPLICATIONS

I. INTRODUCTION

This effort is for the evaluation of a non-toxic photo-catalytic decontamination technology based on silver-exchanged zeolites being developed by the University of Maine research team under the direction of Dr. Howard H. Patterson, Professor, Department of Chemistry, University of Maine, for the destruction of chemical warfare agents. The hypothesis under investigation is that rapid decontamination can be achieved by the interaction of agent with silver metal clusters within zeolites coupled with subsequent photo-catalytic excitation.

The University of Maine program goal was to develop a decontaminant powder to use in the field; therefore, the samples were used as received without drying or modifying. In the as-received state, the samples contain zeolitic water and are considered in a "hydrated" state. Drying or dehydrating the samples would create a different environment.

The primary objective of this test was to evaluate the decontamination efficacy for several silver-doped zeolites against chemical agents to determine the most-active zeolites with or without photo activation.

Summary of Conclusions.

The purpose of this test was to determine the reduction in HD of Ag-exchanged samples compared to the parent material and for samples activated with UV light compared to non-activated samples.

- MCM-141
 - Ag MCM-141 caused a much greater reduction in HD concentration than the parent MCM (~40% reduction versus ~10% reduction in parent material).
 - The effect of UV activation was not tested due to lack of material.
- SOD
 - Amongst four replicates, the parent material showed a greater reduction of HD concentration than the Ag SOD (~40% reduction versus ~20% reduction in Ag material).
 - No observable difference was noted for UV activated SOD versus unactivated. Unactivated Ag SOD caused a slightly greater reduction in HD concentration.

- FAU

- Among three of four replicates, the parent material showed no observable reduction in HD concentration. The Ag FAU showed a greater reduction of HD concentration (~40% reduction).

- No observable difference was noted for UV activated FAU versus unactivated FAU. No observable difference was noted for UV activated Ag FAU versus unactivated Ag FAU.

- AgF1B

- Both AgF1B50 and AgF1B100 showed an approximate 50% reduction in HD concentration.

- No observable difference was noted for UV activated AgF1B versus unactivated AgF1B.

- Ag Zeolite (Aldrich)

- In five of six replicates, Ag Zeolite showed a 50% reduction in HD concentration.

- No observable difference was noted for UV activated Ag Zeolite versus unactivated Ag Zeolite.

2. METHODS AND PROCEDURES

2.1 Test Materials.

The test materials for evaluation are silver-doped zeolites prepared by the University of Maine. Control samples are the parent zeolite before modification. All materials will be used as received. The test materials for the different evaluations are listed in Table 2.1. A sample of the parent starting material needs to be provided for each material type for study. The purpose of the parent starting material is to provide a control / reference sample to compare the silver-exchanged material performance.

As outlined in Table 1, three pairs of parent and silver-doped zeolites were provided. In addition, a fourth set, labeled AgF1b was also provided. This set was compared to a Silver-Exchange Zeolite purchased from Sigma-Aldrich (382280).

| Table 1: Test Materials | |
|--------------------------------|------------------------|
| Material | Amount Provided |
| MCM-41, Parent | 0.5 grams |
| Ag-MCM-41 | 0.25 grams |
| SOD, Parent | 1 gram |
| Ag-SOD | 1 gram |
| FAU, Parent | 10 grams |
| AgF1B25 | 0.2 grams |
| AgF1B50 | 0.2 grams |
| AgF1B100 | 0.2 grams |
| Ag-Zeolite (Aldrich) | 25 grams |

2.2 Agents and their Surrogates.

The chemical agent surrogate 2-chloroethyl phenyl sulfide (CEPS) was purchased from Sigma-Aldrich (catalog #417602, CAS #5535-49-9). Agent testing was performed using HD obtained from ECBC Chemical Transfer Facility (lot # HD-U-2325-CTF-N).

2.3 Extraction Tests.

Extractions were performed in small glass Petri dishes to eliminate some solvent compatibility issues. To further that end, chloroform was selected as the choice solvent for its stability and known extracting capacity. Tests were performed by placing 5 2- μ L drops of agent on the bottom of the Petri dish. A mass of 0.2 g of zeolite powder was poured over the top of the drops. To ensure maximum contact between zeolite and agent, the dish was lightly swirled. The dish was covered and either placed in the ATS light box, or was left in the hood for a period of 20 min. Following this exposure time, the dish was extracted with 20 mL of chloroform. The resulting mix was stirred with a pipette tip, and then filtered with a glass fiber filter into a GC vial. The filter removed the zeolite powder from the solution, which would otherwise inhibit GC performance.

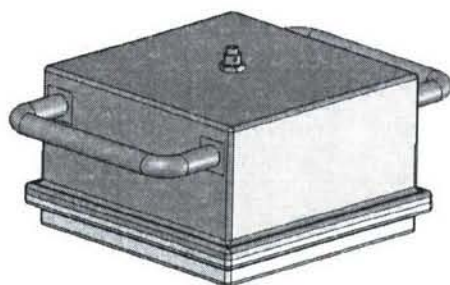
2.4 Gas-Chromatography Analysis.

Following extraction, samples were analyzed using a Gas-Chromatography Flame Ionization Detector (GC-FID). Standards were prepared daily in chloroform to provide accurate instrument calibration. Daily calibration included 6 levels: 2.5, 5, 25, 50, 150, and 500 μ g/mL. The calibration curve was linear, with the origin ignored. Solvent blanks were run before and after each sample set.

2.5 UV Light Source.

Applied Thermal Sciences, Inc provided the UV light source designed with both safety and functionality in mind. The interlock switch prevented unintentional activation of the source. Likewise, it provided a precise delivery of the 200 hz output with +5V amplitude for a set period of time. The emitted light was pulsed from the xenon source.

Figures 1 – 3 provide a graphic overview of the light system and its associated features. Not shown is a timer which was set to deliver 20 min of light before resetting.



Lipped Edge Designed
to Prevent UV-light
from Escaping Light Box

FIGURE 1 Light Box, Side View

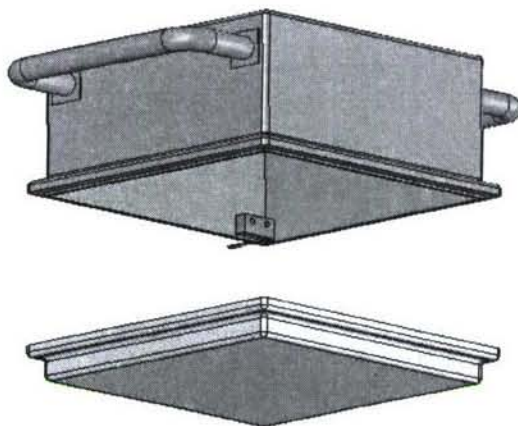
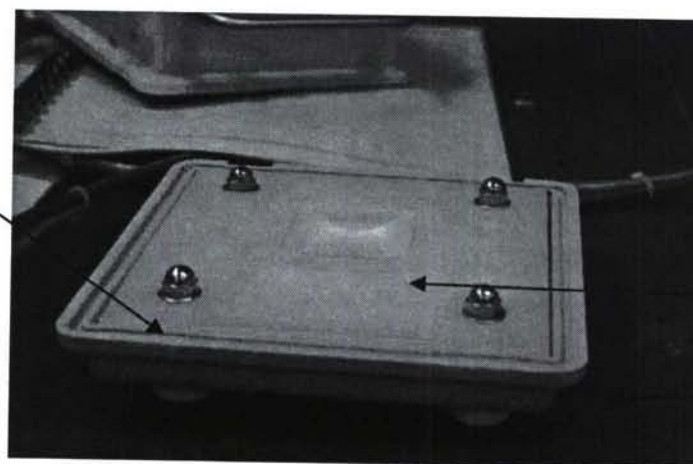


FIGURE 2 Light Box, Switch View

Sample Contained
Here



“Cover”

Interlock Switch

“Base”

FIGURE 3 Light Box, Base with Weigh Boat, Photo

2.6 Types of Testing.

Scoping Tests: The scoping tests were conducted for method development and to determine any incompatibilities or likely challenges prior to commencing testing.

Chemical Agent Simulant Screening: Some test samples were screened using chemical agent simulant CEPS. These tests were conducted with and without light activation and provided further information for testing protocol.

Chemical Agent Tests: All samples provided were tested against chemical agent HD. Tests were conducted with and without light activation, where sufficient sample was provided.

2.7 Test Matrix.

Table 2 outlines which of the samples provided were included in NMR and Extraction tests.

| Table 2: Test Matrix | | |
|----------------------|------------------------|-------------------------|
| Material | Extraction w/ light | Extraction w/o light |
| MCM-41, Parent | ✓ | |
| Ag-MCM-41 | ✓ | |
| SOD, Parent | ✓ | ✓ |
| Ag-SOD | ✓ | ✓ |
| FAU, Parent | ✓ | ✓ |
| Ag-FAU | ✓ | ✓ |
| AgF1B25 | | |
| AgF1B50 | | ✓ |
| AgF1B100 | ✓ | |
| Ag-Zeolite (Aldrich) | ✓ | ✓ |

3. EXTRACTION TEST RESULTS AND DISCUSSION

Ten microliters of HD was delivered and extracted in 20 mL of chloroform. The density of HD is 1.268 g/mL for an applied concentration of 634 µg/mL (see section 6.0 for calculations). Percent recovery was calculated as concentration of sample solution divided by concentration of daily HD control sample, where available. On 5/4/2006, when no control was prepared, adjusted percent recovery was calculated against the average HD control concentration of 682 µg/mL.

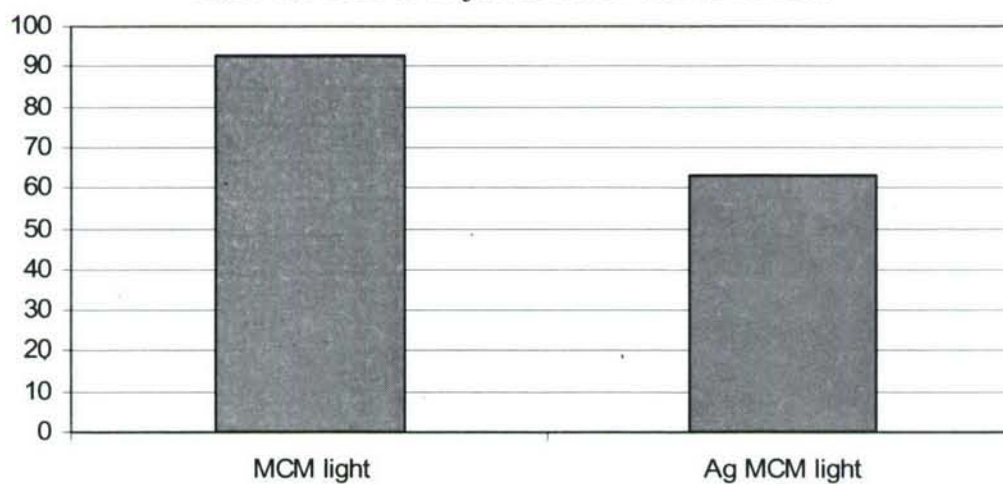
Table 3 provides results at a glance. Results are given as averages of adjusted percent recoveries. In depth results analysis is broken down in subsequent sections.

| Table 3: Summary of Extraction Results | | | | |
|---|----------------------------|------------------------|-----------------------------|------------------------|
| Material | Extraction w/ light | # of Replicates | Extraction w/o light | # of Replicates |
| MCM-41, Parent | 93% | 1 | | 0 |
| Ag-MCM-41 | 63% | 1 | | 0 |
| SOD, Parent | 64% | 3 | 67% | 3 |
| Ag-SOD | 113% | 1 | 90% | 3 |
| FAU, Parent | 90% | 2 | 76% | 2 |
| Ag-FAU | 57% | 1 | 62% | 1 |
| AgF1B25 | | 0 | | 0 |
| AgF1B50 | | 0 | 54% | 1 |
| AgF1B100 | 53% | 1 | | 0 |
| Ag-Zeolite (Aldrich) | 55% | 4 | 65% | 4 |

3.1 MCM + HD Results.

Due to the limited amount of MCM and Ag-MCM, only one test was done with each. On 5/4/2006, samples were prepared and exposed to UV light for 20 min. The two samples were subsequently extracted and compared to the daily control sample. As shown in Table 4, the MCM showed a 10% of the HD whereas the Ag-MCM sample showed nearly 40% reduction of the HD compared to the control sample.

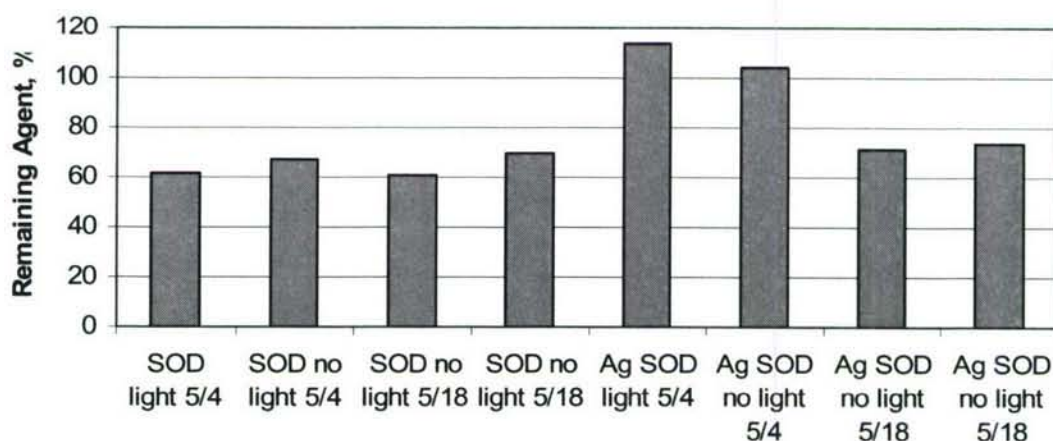
Table 4: MCM % Adjusted Recoveries 5/10/2006



3.2 SOD + HD Results.

Testing on SOD and Ag-SOD was conducted on 5/4/2006 and 5/18/2006. On 5/4/2006, both SOD and Ag-SOD were tested with and without the use of UV light. Two more replicates of each SOD and Ag-SOD without UV light were conducted on 5/18/2006. As shown in Table 5, the SOD experienced about a 40% reduction in HD concentration. The Ag-SOD samples showed no observable reduction in HD concentration, with or without UV light activation on 5/4/2006, but nearly a 30% reduction in HD concentration on 5/18/2006. No control sample was prepared on 5/4/2006.

Table 5: SOD % Adjusted Recoveries 5/4/2006* & 5/18/2006

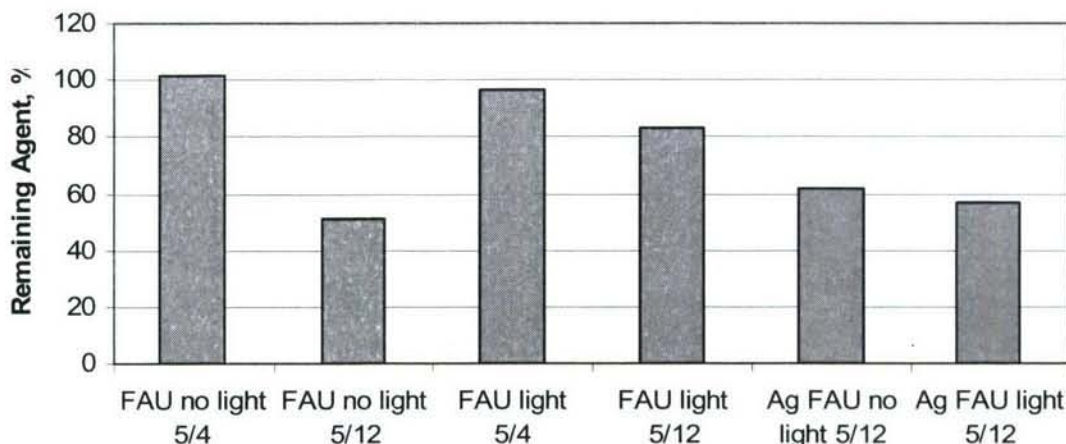


* No HD control was used on this test date. Adjustment to concentration in comparison to average control concentration.

3.3 FAU + HD Results.

On 5/4/2006, FAU was tested both with and without UV light. Both FAU and Ag-FAU were again tested both with and without light activation on 5/12/2006. Table 6 provides the adjusted percent recoveries. The light activated FAU samples showed a slight reduction in HD concentration; however, that reduction may be within test error and not be significant. The FAU samples showed no observable reduction in HD concentration without UV light activation on 5/4/2006, but nearly a 50% reduction in HD concentration on 5/12/2006. Ag FAU showed a 40% reduction in HD concentration regardless of exposure to UV light. The 5/12/2006 control was analyzed at 116% the concentration of the applied concentration. No control sample was prepared on 5/4/2006.

Table 6: FAU % Adjusted Recoveries 5/4/2006* & 5/12/2006



* No HD control was used on this test date. Adjustment to concentration in comparison to average control concentration.

3.4 AgF1B + HD Results.

Due to the limited amount of AgF1B50 and AgF1B100, only one test was done with each. On 5/15/2006, AgF1B50 was prepared and allowed to age for 20 min. AgF1B100 was prepared and exposed to UV light for 20 min. The two samples were subsequently extracted and compared to the daily control sample. As shown in Table 7, the AgF1B50 and the AgF1B100—exposed to UV—had very similar HD reductions at about 50%, when compared to the control sample. The control was analyzed at 94% the concentration of the applied concentration.

3.5 Ag-Zeolite (Aldrich) + HD Results.

Testing on Ag-Zeolite (Aldrich) was conducted on 5/4/2006 and 5/18/2006. On 5/4/2006, Ag-Zeolite was tested with and without the use of UV light. As shown in Table 8, the Ag-Zeolite that was left outside the light box showed about a 10% reduction in HD concentration, and the one that was exposed to UV light experienced about a 45% reduction in HD concentration, when compared to the average control concentration. No control sample was prepared on 5/4/2006.

Table 7: AgF1b % Adjusted Recoveries 5/15/2006

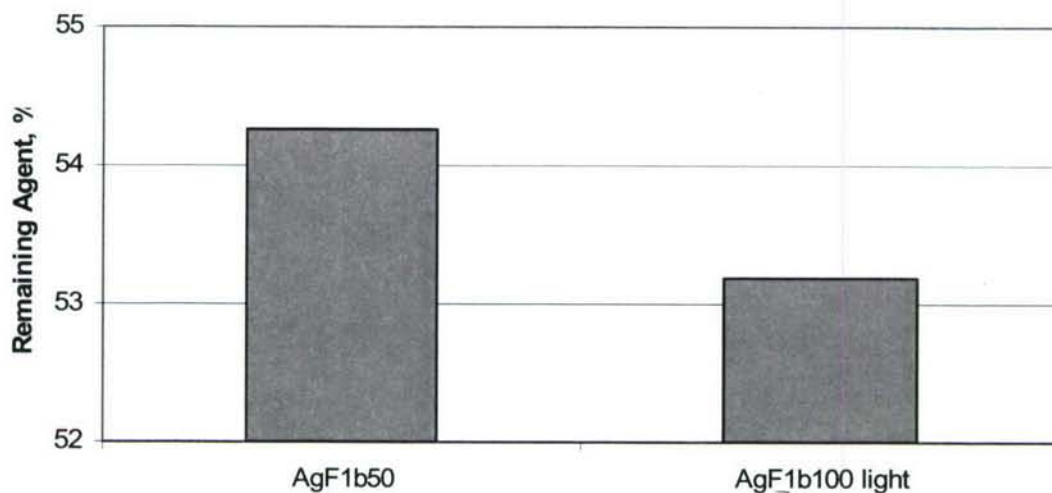
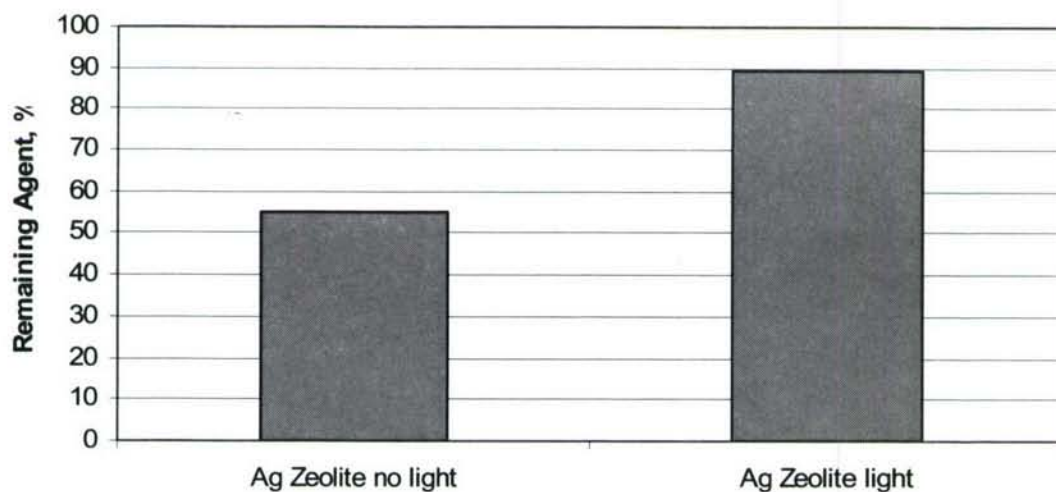


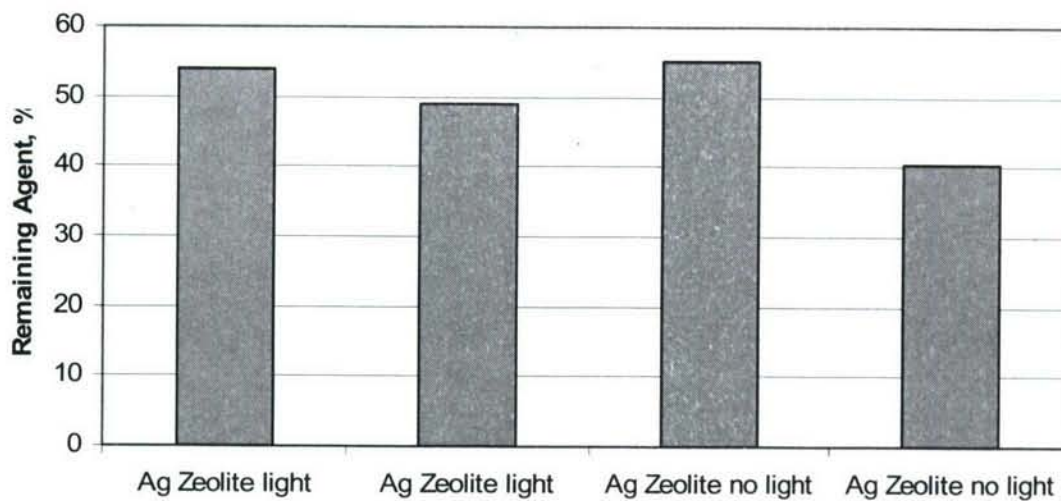
Table 8: Ag Zeolite % Adjusted Recoveries 5/4/2006*



* No HD control was used on this test date. Adjustment to concentration in comparison to average control concentration.

Two more replicates of each Ag-Zeolite with and without UV light were conducted on 5/18/2006. Table 9 provides results of this study. The zeolites showed a reduction of approximately 50% for both the activated and unactivated Ag Zeolites. These values are in comparison to the two controls, which were analyzed at 100 and 107% of the applied concentration.

Table 9: Ag Zeolite % Adjusted Recoveries 5/18/2006



3.6 Discussion.

Due to the limited quantity of several zeolites, it was difficult to perform sufficient replicates to provide statistically significant extraction results. The MCM set, tested on 5/10/2006, suggests a greater HD reduction by the silver zeolite; however, variation in spike volumes might also explain the difference. Concentrations of the MCM sample exposed to light, the Ag-MCM sample exposed to light, and the HD control sample were 709-, 485-, and 766- $\mu\text{g/mL}$, respectively. When compared to the control sample, the adjusted percent reduction is approximately 10 and 40%. However, when compared to the applied concentration, this drops to -10 and 24% reduction.

GLOSSARY

| | |
|-----------|--|
| APG | Aberdeen Proving Grounds |
| ATS | Applied Thermal Sciences, Inc. |
| CB | chemical and biological |
| CofA | certificate of analysis |
| CT | concentration time |
| CW | chemical warfare |
| DoD | Department of Defense |
| DS | Decontamination Sciences |
| ECBC | Edgewood Chemical and Biological Center |
| hr or hrs | hour or hours |
| IAW | in accordance with |
| IOP | Internal Operating Procedure |
| min | minutes |
| MSDS | Material Safety Data Sheets |
| PI | principal investigator |
| PPE | personal protective equipment |
| Pre-Op | pre-operational |
| R&D | Research and Development |
| RDECOM | Research, Development, and Engineering Command (formerly SBCCOM) |
| RRO | Risk Reduction Office |
| SD | standard deviation |
| SOPs | standing operating procedures (standard also used with the same meaning) |
| SOR | start of run |
| t | time |

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APPENDIX

CALCULATIONS

Concentration of solution if decontamination does not occur:

| | | | |
|-----------------|----------------------|----------------------------|----------------------|
| 10 μ L HD | 1 mL 1000 μ L | 1.268 g mL | 0.01268 g HD |
| 0.01268 g HD | 1000000 μ g g | 20 mL CHCl ₃ | 634 μ g HD mL |